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MASS TRANSFER INTO NON-NEWTONIAN SYSTEMS

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FINAL PROGRESS REPORT

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MASS TRANSFER INTO NON-NEWTONIAN SYSTEMS

Covering Twenty-Four Month Period From
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STATEMENT OF PROGRESS

A. Theses and Publications

1. Thesis - This report

The following thesis has been accepted and published during the past year.

- a. "A Study of Diffusivity into Non-Newtonian Slurries," by G. A. Strobel, Thesis, Master of Science, Cornell University, Ithaca, N.Y., June, 1965.

2. Publications - This report

The following paper has been given since the last report.

- a. "Mass Transfer into Non-Newtonian Fluids" by V.C. Behn and G.A. Strobel. Given before the Rheology Conference sponsored by the Department of Mechanical and Aerospace Engineering, Syracuse University, August 23 to 27, 1965 at Pinebrook, N.Y. To be published by Academic Press.

Ten copies of this paper will be forwarded to USPHS as soon as it is published. A copy of the paper is given in Appendix A.

In addition, in my capacity as member of the Task Committee on Non-Newtonian Flow of the ASCE, I have been asked to give a paper called Non-Newtonian Flows in Sanitary Engineering before the Water Resources Conference of the ASCE in Denver, May 19, 1966.

3. Thesis and Publications - Previous reports

The following have been reported in previous progress reports.

- a. "The Determination of the Flow Parameters of Waste Sludges by Means of a Capillary Viscometer" by J.M. Sirman, Thesis, B.S. with Distinction in Civil Engineering, University of Delaware, Newark, Delaware, July, 1960.
- b. "Fundamental Rheological Properties of Sewage Sludges," by D.R. Tatman, Thesis, Master of Civil Engineering, University of Delaware, Newark, Delaware, June, 1961.
- c. "The Effect of Shear Rate Upon Diffusion Coefficients for Non-Newtonian Fluids" by H.E. Read, Thesis, Master of Mechanical Engineering, University of Delaware, Newark, Delaware, June, 1961.
- d. "Flow Equations for Sewage Sludges" by V.C. Behn, Jour. Water Pollution Control Federation, 32, No. 7, p. 728, July, 1960.

- e. "Determination of the Flow Parameters of Sludge" by J.M. Sirman, Water and Sewage Works, 107, No. 11, p. 417, November, 1960.
- f. "Derivation of Flow Equations For Sewage Sludges" by V.C. Behn, Paper 2663, Jour. Sanitary Engineering Div., Proc. A.S.C.E., Vol. SA6, November, 1960.
- g. "Application of the Method of Composition and Linear Regression Analysis to a Problem Involving a Pseudo-plastic Suspension" by W.F. Ames and V.C. Behn, Trans. Society of Rheology, V, p. 53, 1961.
- h. "Experimental Determination of Sludge-Flow Parameters" by V.C. Behn, Jour. Sanitary Engineering Div., Proc. A.S.C.E., 88, SA3, p. 39, May, 1962.
- i. "Diffusion in Slurries and in Non-Newtonian Fluids" by S.B. Clough, H.E. Read, A.B. Metzner, and V.C. Behn, A.I.Ch.E., Jour., 8, No. 3, p. 346, July, 1962.
- j. "Mass Transfer into Non-Newtonian Fluids" by M.J. Bellanca, Thesis, Master of Science, Cornell University, Ithaca, N.Y., February, 1964.
- k. "Capillary Versus Pipeline on Determining Flow Behavior of Digested Sewage Sludge," by V.C. Behn and R.M. Shane, Water and Sewage Works, 110, No. 7, pp. 272-274, July, 1963.

B. Results Obtained

Originally, this project was concerned with the fundamental rheological properties of sewage sludge. Thus, in the list of publications in paragraph A.3 articles d. and f. were concerned with a mathematical review of the application of non-Newtonian technology to the transport of sewage sludges. Article e. was concerned with obtaining experimental data with a capillary viscometer. Article g. reported similar work with a rotational viscometer and gave a method for analyzing the data. Article h. gave experimental results on sludge flow parameters, reporting on such influences as temperature and dissolved gasses.

The original objectives having been met, focus of this project was turned to the question of the non-Newtonian properties of waste suspensions as they would influence mass transfer. Article i. in paragraph A.3 was concerned with diffusion into non-Newtonian slurries. The objectives formulated, using article i. as a point of departure, were to determine the rate of diffusion of benzoic acid into an activated sludge solution, and to determine if the correlations used for Newtonian could be extended to the non-Newtonian case by making appropriate corrections. In general it was found that an activated sludge actually would chemically adsorb benzoic acid, while in the correlations an adjustment in the Reynold's Number sufficed.

In plans for the future of the preceding progress report, it was mentioned that diffusivity of benzoic acid would be checked against concentration of clay slurry. The results of this study are given in Appendix A. In general we found that diffusion into a medium

containing a significant content of suspended clay actually increased. Since the saturation concentration of benzoic acid into clay-water solutions did not increase, there was no reason to suspect that this was due to adsorption of benzoic acid by the clay material. Apparently there is an effect due to the particles of clay which remains obscure at this writing.

APPENDIX A

Mass Transfer Into Non-Newtonian Fluids

by Vaughn C. Behn and Gerald A. Strobel, School of Civil Engineering, Cornell University, Ithaca, New York

Introduction

The work described in this report is concerned with a study of diffusion of benzoic acid at constant temperature into kaolinite slurries of varying concentration (1). Diffusivities were obtained by recirculating the non-Newtonian slurry under laminar flow conditions through a soluble cast tube of benzoic acid. The diffusivity of benzoic acid was then calculated utilizing the Leveque assumption that under laminar flow conditions the mass of benzoic acid will penetrate only a small distance into the slurry (2). The values of diffusivity of benzoic acid into suspensions of 10, 15, 20, and 25% by weight kaolinite could then be compared with that into water at the same temperature (approximately 20°C). The formula to be used in comparing the diffusion into a non-Newtonian suspension with that of water was presented by Clough et al. (3). This formula is in effect an extension of Eyring's rate theory of mass transfer.

Theory

The basic differential equation for material diffusing into a flowing liquid in a cylinder is:

$$u \frac{\partial c}{\partial z} = D \left[\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right] \dots \dots \dots (1)$$

where u = local fluid velocity, LT^{-1}

z = longitudinal coordinate of mass transfer system, L

r = radius coordinate of mass transfer system, L

D = diffusivity, L^2T^{-1}

c = concentration, ML^{-3} .

In the case involving heat transfer, Leveque made the assumption that the value for the local velocity, u , could be substituted for by a constant, α , times the distance y travelled in diffusing:

$$u = \alpha y \quad \dots \dots \dots (2)$$

where $y = r_w - r$, r_w being the actual radius of the pipe in which diffusion was taking place.

For a non-Newtonian fluid α is the shear rate at the wall:

$$\alpha = \frac{8V}{d} \frac{(3n'+1)}{4n'} \quad \dots \dots \dots (3)$$

where V = mean velocity of flow, LT^{-1}

d = diameter of capillary, L

n' = flow behavior index for fluids of unspecified shear rate - shear stress relationship, Dimensionless.

Combining these equations with the Whitman model for K_L , the liquid film coefficient, results in the equation

below for calculating diffusivity of benzoic acid into the kaolinite suspension (2):

$$D_{nn} = \frac{1}{L} \left(\frac{\rho}{w\delta} \right)^{1/2} \left(\frac{V_f}{5.5t_r} \right)^{3/2} \left(\ln \frac{C_s - C_i}{C_s - C_f} \right)^{3/2} \dots (4)$$

where D_{nn} = diffusivity into a non-Newtonian fluid,
 L^{2-1-1}

L = tube length, L

ρ = fluid density, ML^{-3}

w = fluid mass rate, MT^{-1}

V_f = fluid volume, L^3

t_r = time of diffusion run, T

C_s, C_i, C_f = saturation, initial, and final values
of concentration, ML^{-3}

$$\delta = \frac{\alpha}{8V/d} = \frac{3n'+1}{4n'}, \text{ Dimensionless}$$

The diffusivities calculated by equation (4) were then compared with an equation presented by Clough et al. which is an extension of Eyring's rate theory of mass transfer (3). Clough et al. have written the following equation for diffusion into a non-Newtonian fluid, where the fluid contains inert suspended solids:

$$D_{nn} = \sum_{n=1}^N \chi_n D_n = \chi_{cp} D_{cp} \dots (5)$$

where χ is the volume fraction occupied by each particular phase of the non-Newtonian fluid, and the subscript cp refers to the continuous phase of the suspension not occupied by any suspended particles.

Now Ree and Eyring had previously offered the following expression for diffusion into a Newtonian solution (4:98):

$$D = \frac{kT k'}{\lambda \xi k'' \mu} \cdot \frac{d \ln a}{d \ln c} \quad \dots \dots \dots (6)$$

where D = diffusivity into Newtonian fluid

T = absolute temperature

k = Boltzmann's Constant

k'k'' = specific reaction rates in the solution
and pure liquid

μ = viscosity

λ = distance of two equilibrium positions for
flow in direction of shear

a = activity

c = concentration

ξ = number of viscous shears of neighboring
molecules whose movement is opposite to that
of diffusing molecule.

The ratio of D_{nn} to D can be found by using equations (5) and (6), assuming that the ratio of the reaction rates, activities, and the concentrations would be approximately one:

$$\frac{D_{nn}}{D} = \chi_{cp} \frac{\xi}{\xi_{cp}} \frac{\mu}{\mu_{cp}} \quad \dots \dots \dots (7)$$

In equation (7) the subscript cp refers to the continuous phase. The ratio ξ/ξ_{cp} represents the number of

viscous shears in water to that in the continuous phase. μ/μ_{cp} represents the viscosity reached at very high shear rates. χ_{cp} is the fractional volume of the continuous phase. As such χ_{cp} is difficult to calculate with precision because the actual amount of hydration of the suspension is unknown. Nevertheless, a figure can be assigned to it with some reliance. This means that the quantity ξ/ξ_{cp} is the remaining unknown in equation (7). When values of this ratio are calculated equation (7), if correct, can be used to solve for diffusivities into non-Newtonians.

Experimental Apparatus

As shown in Figure 1, the experimental model used was a system where the kaolinite slurry was recirculated in laminar motion at a constant 20°C through a soluble cast tube of benzoic acid. The inside diameter of the benzoic acid tube was 1/2" and the length was 18". After the tube the mixture went to a 5 liter fluid reservoir with stirrer. The material was pumped by a Sigmamotor Pump No. T65 through a flowmeter to the benzoic acid tube.

Prior to each run, the rheological properties of the kaolinite suspensions had to be established. The value of n' for each % by weight of kaolinite was found using the experimental arrangement shown in Figure 2 (5).

Details of the experimental equipment used are available (1) (2). All of the test runs were conducted in a constant temperature room at approximately 20°C.

Experimental Procedure

The slurry samples were prepared by drying a sample of kaolinite at 103°C . The sample was then weighed and added to a predetermined weight of distilled water. The suspensions used in this study were 10, 15, 20, and 25% kaolinite by weight. It should be noted here that a 5% solution was prepared, but it was found to become turbulent at relatively low rates of shear and was not used.

The kaolinite suspensions were then tested in the capillary viscometer and found to be slightly thixotropic. That is to say some variation of n' occurred with varying capillary tube. Nevertheless, it was felt that results within experimental error could be obtained with a .216 cm diameter by 153.1 cm length tube. We followed the procedure of Read (2) in allowing at least one hour of recirculation before running the test to calculate n' .

The saturation of kaolinite suspension was found by allowing the suspension to circulate through the diffusion system until three successive kaolinite samples showed no change in benzoic acid concentration.

The mass transfer tests, involving the set of data in equation (4), were run on each of the four benzoic acid concentrations. Further details are given in the thesis by Strobel (1).

Experimental Results

The suspension flow parameters are given in Table 1, the saturation concentration of benzoic acid in kaolinite to suspension in Table 2, and the diffusion parameters are given in Table 3. In comparing D_{nn} given in Table 3 with

D, the diffusion of benzoic acid into water a value of $D = 0.9 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ was used (1). Also the viscosity of water was taken as $\mu = .01$ poises. To find μ_{cp} we took the viscosity of the suspension of an inverse of shear rate equal to zero (3).

Discussion

First as regards Table 1, it is apparent that we obtained a truly wide range of non-Newtonian behavior with the value of n' equal to 0.802 at 10% kaolinite suspension to $n' = 0.306$ at 25% concentration. From Table 2 we conclude that the concentration of kaolinite does not influence the saturation concentration of benzoic acid. Generally speaking there is a diminution in concentration as one goes from 15 to 25% kaolinite. In other words we can support Read's findings that there was no adsorption taking place (2).

This leaves us with Table 3 or Figure 3. Table 3 says that instead of decreasing with increasing slurry concentration the actual value of D_{nn} was found to increase. In other words for kaolinite concentrations of 10 to 25% by weight, D_{nn} varied from 3.05 to $3.77 \times 10^{-5} \text{ cm}^2/\text{sec}$.

If we take up consideration of the ratio ξ/ξ_{cp} we see that the calculated value ranges from 3.98 to 9.21 with an increase in concentration of from 10 to 25%. If ξ for pure water is taken as 15 (3), then ξ_{cp} must decrease from 3.98 to 1.6 for the increase from 10 to 25% in kaolinite. Perhaps then we can assume that the diffusing species is mainly associated with the suspending particles. But there is no evidence for this association, and in fact there is the

evidence above cited with respect to solubilities that there is no association.

We conclude from this that equation (7) is not sufficient to explain the results obtained. The findings of an increased diffusivity could be explained by either turbulent flow or adsorption of the benzoic acid molecule on the clay, but we do not believe that either of these factors were present. A factor involving the motion of the clay particles might serve to answer the problem, but our results, as well as previously reported data (3), do not indicate that the diffusion is a function of the shear rate. Astarita has reported in some diffusion data involving a gas taken up by a non-Newtonian liquid (6). He notes that similar to our data he gets D_{nn} values which are higher than D . Metzner has tentatively suggested that the suspension may in fact be structured in such a manner as to permit regions of high diffusivity in the immediate vicinity of the added particles (7). In any case the basic notion that diffusion rates increase with the presence of suspended material is an extremely interesting one.

Summary and Conclusions

This report considers diffusivity of benzoic acid into kaolinite slurries of varying concentration. The interesting aspect of the experimental work is the ratio of diffusion into kaolinite suspension, D_{nn} , to that into water, D , varied from 3.05 to $3.77 \times 10^{-5} \text{ cm}^2/\text{sec}$ as the kaolinite concentration increased from 10 to 25%. The values were then used to calculate ξ/ξ_{cp} which fell off much too rapidly. This would

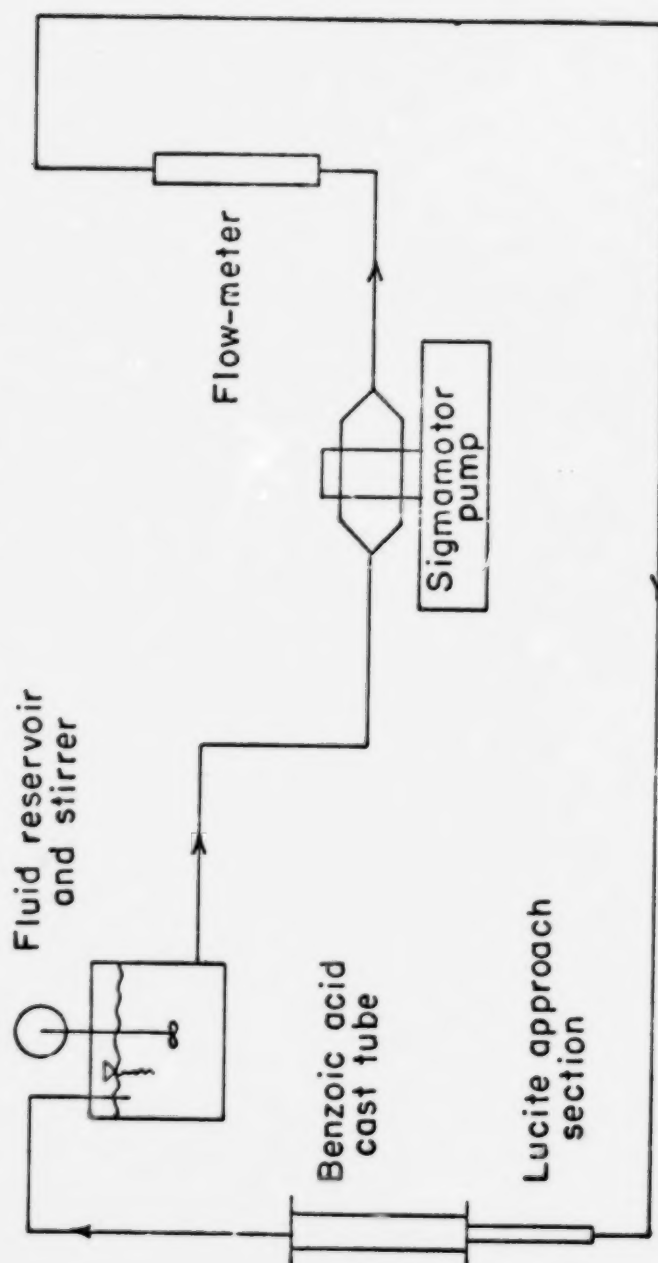
assume that the diffusing species is mainly associated with the suspending particle, but since there was also a decrease in saturation concentration with increasing kaolinite concentration we do not believe there was any assimilation of the benzoic acid by the clay. We are still seeking means to explain this data.

Acknowledgement

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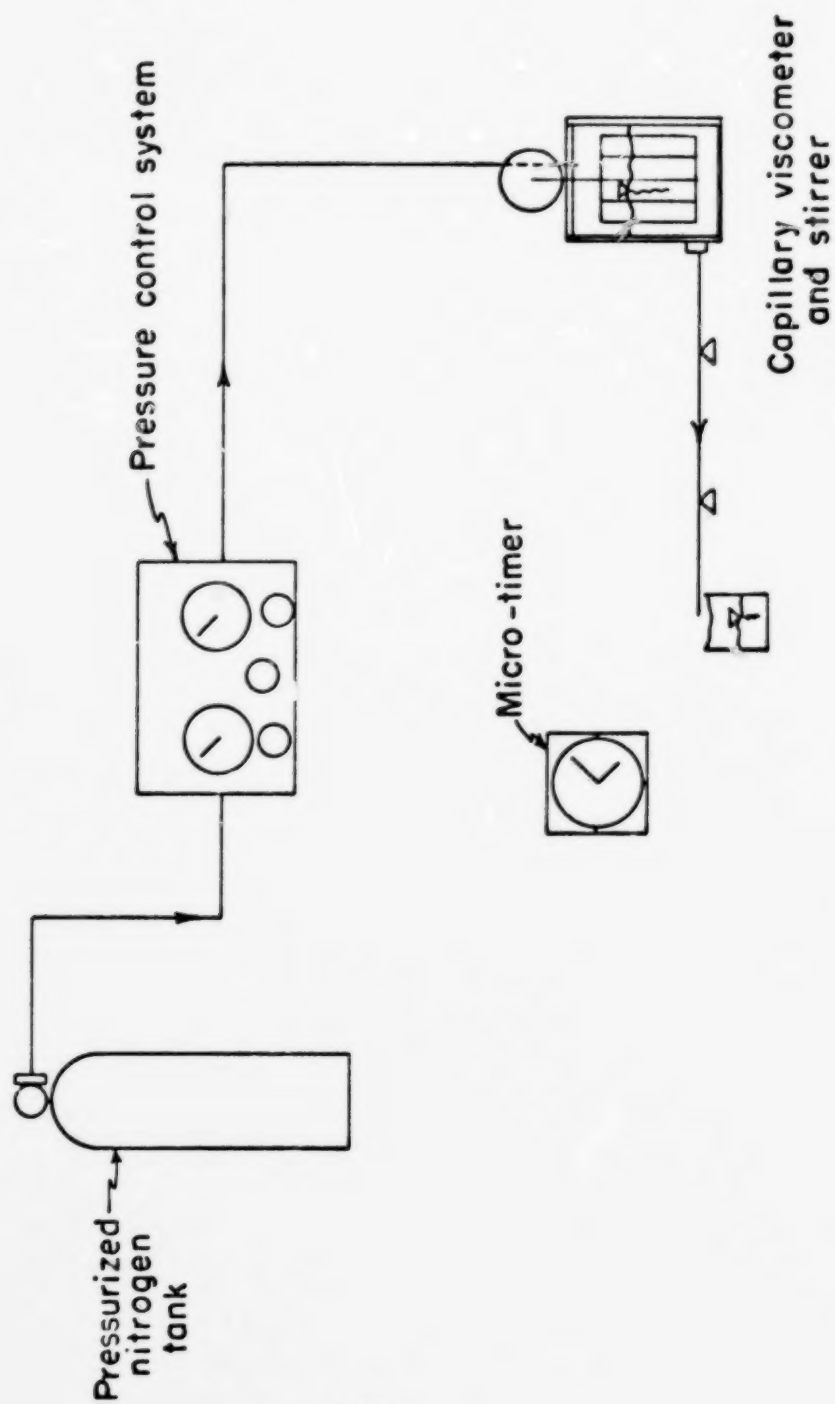
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All connections made with tygon tubing

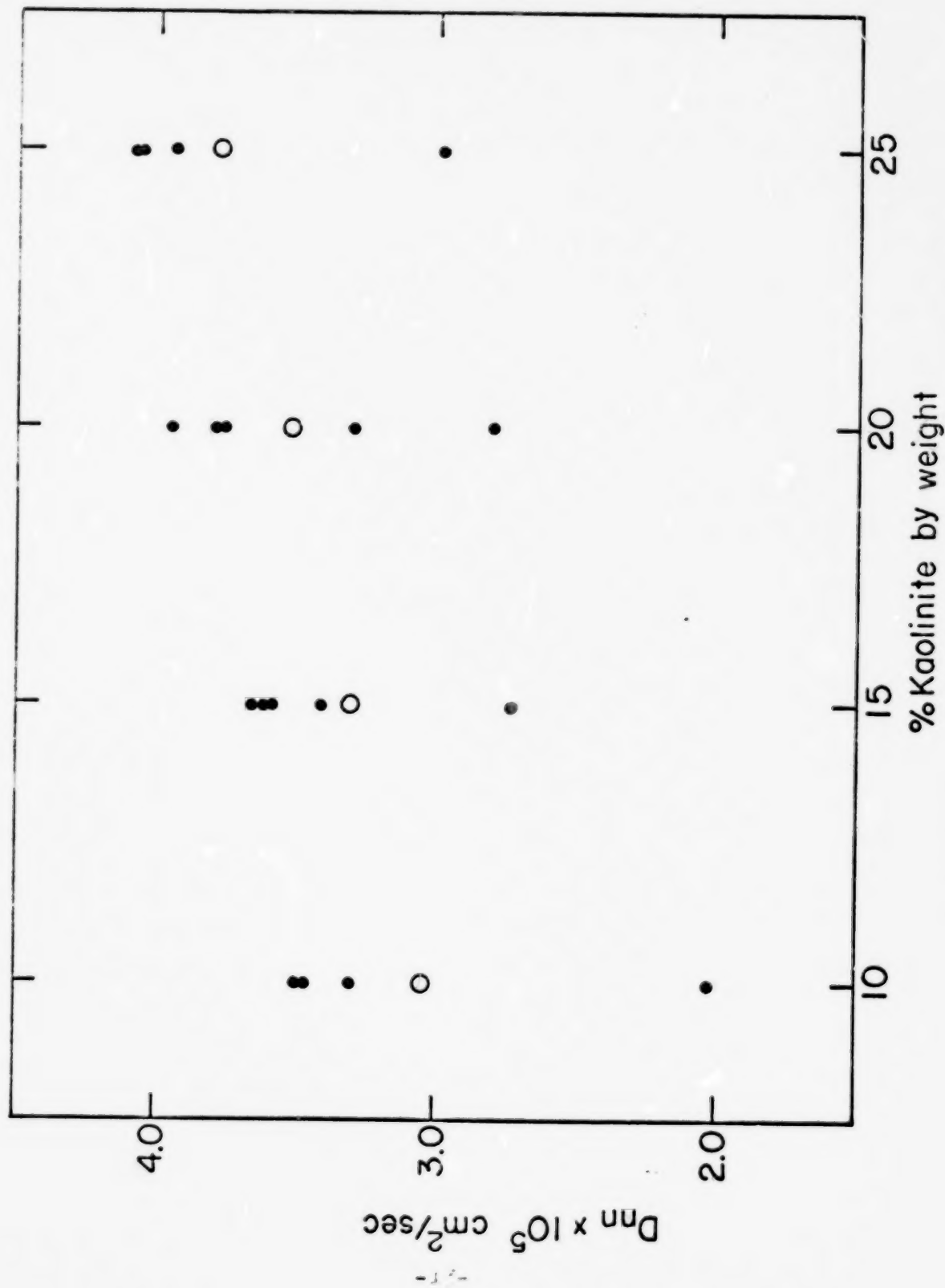
FLOW DIAGRAM FOR MASS TRANSFER SYSTEM

FIGURE 1.



FLOW DIAGRAM FOR VISCOMETRIC SYSTEM

FIGURE 2.



DIFFUSIVITY VERSUS CONCENTRATION

TABLE 1.

Slurry flow parameters

Conc. % kaolinite by wt.	n'	Density gms./cc
10%	0.802	1.065
15%	0.663	1.105
20%	0.574	1.141
25%	0.306	1.187

TABLE 2.

Saturation concentration of benzoic
acid in kaolinite slurry

Conc. % kaolinite by wt.	Temp. °C	Sat. conc. benzoic acid gm./liter
10 %	20.5	2.510
	21.0	2.460
15 %	20.0	2.543
	21.5	2.558
20 %	20.0	2.506
	22.0	2.543
25 %	21.0	2.485
	21.5	2.516

TABLE 2.

Diffusion parameters for kaolinite slurries

Conc. % kaolinite by wt.	$D_{nn} \times 10^5$ cm^2/sec	X_{cp} %	μ_{cp} poises	ξ/ξ_{cp}
10%	3.05	91.8	.0120	3.98
15%	3.40	90.4	.0140	5.86
20%	3.52	89.3	.0198	8.73
25%	3.77	86.4	.0220	9.21